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# Effects of plasma gas composition on bond strength of hydroxyapatite/titanium composite coatings prepared by rf-plasma spraying

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## Abstract

The effects of plasma gas composition on the bond-strength of HA/Ti composite coatings were investigated. HA/Ti composite coatings were deposited on titanium substrates by a radio-frequency (rf) thermal plasma spraying method with input powers of 10–30 kW. The ratio of the HA and Ti powders supplied into the plasma was precisely controlled by two microfeeders so as to change the coating's composition from Ti-rich at the bottom to HA-rich at its upper layer. The bond (tensile) strength of the obtained HA/Ti composite coatings was 40–65 MPa when sprayed with plasma gas containing $N_2$ (i.e., Ar–$N_2$). On the other hand, HA/Ti composite coatings prepared with plasma gas containing $O_2$ (i.e., Ar–$O_2$) had significantly lower bond strength (under 30 MPa). XRD patterns of Ti coatings without HA showed that titanium nitride and titanium dioxide formed, respectively, on titanium deposits sprayed with Ar–$N_2$ and Ar–$O_2$ plasma. Scanning electron microscopic (SEM) observation showed an acicular texture on the Ti deposits prepared with Ar–$N_2$ plasma. SEM observations implied that, when sprayed with Ar–$O_2$ plasma, a thin $TiO_2$ layer formed at the interfaces between the Ti splats in the deposits.

*Keyword:* Hydroxyapatite/titanium; Composites; Mechanical properties; Biomedical application

## 1. Introduction

Plasma-sprayed hydroxyapatite ($Ca_{10}[PO_4]_6[OH]_2$; HA) coatings on titanium alloy implants have been used for medical applications to promote the osteoconductivity of implanted materials.[1–3] For practical medical applications, such as orthopedic implants, HA coatings with excellent substrate adhesion have been strongly demanded to provide long-time fixation.[3] It is also particularly important for biomaterial applications that such HA coatings should not be contaminated by toxic materials. The radio-frequency (rf)-thermal plasma spraying (TPS) method has an advantage over the direct current (dc)-TPS method since the contamination of HA coatings by toxic materials, such as copper and tungsten compounds used for electrodes, can be avoided.[4] However, due to the large difference in physical properties, including thermal expansion coefficients, specific heat and elastic modulus, between the ceramic coating and the metal substrate, residual stress arises at the ceramic/metal interface, as has been reported in the case of DC-TPS.[5,6] This residual stress often causes cracks and reduces the bond strength of ceramic coatings. For this reason, the bond strength of plasma-sprayed HA coatings on Ti-6Al-4V alloy significantly decreases with increasing coating thickness.[7]

Recently, we have developed a gradual composite coating method employing rf-TPS that provides strong adhesion between HA coatings and titanium (Ti) substrates.[8,9] Moreover, we have reported that the in situ nitriding of Ti particles by reactive-plasma spraying (RPS), a variation of plasma spraying, improves the bond strength of HA/Ti composite coatings.[10,11] During RPS, plasma-enhanced reactions between Ti particles and the reactive gaseous species present in the plasma flame produce various in situ synthesized phases on the surface of the Ti particles. Therefore, the effects of the processing parameters on the bond strength of HA/Ti composite coatings prepared by the RPS method may differ from those on pure HA coatings. In this study, the

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effects of plasma-enhanced reactions between the Ti powder and the plasma gas on the adhesiveness of deposited HA/Ti composite coatings are discussed in terms of the microstructure and phases formed on the coatings. In particular, the influence of in-flight reactions of the Ti particles in plasma flame containing either nitrogen or oxygen were investigated.

## 2. Methods

A thermal plasma was generated at a frequency of 4 MHz and at an input power of 10–27 kW. Our rf-RPS processing parameters are summarized in Table 1. In the present study, we used plasma gas compositions containing Ar and either 1–6% $O_2$ or 1–6% $N_2$. The plasmas generated using these gas compositions shall be referred to hereafter as Ar–$O_2$ and Ar–$N_2$ plasma, respectively. We employed an rf-RPS apparatus with a 4 MHz-35 kW power source (Nihon Koshuha Co., Ltd., Japan) and two powder feeders (AM-30-3L, Technoserve Co., Ltd., Japan). Our technique for preparing the HA/Ti composite coatings is based on precise control of the starting material's composition using two microfeeders which make it possible to feed the HA and Ti powders at an accurate rate.[8,9] The starting material's composition was regulated so as to change the composition of the coating gradually from Ti-rich at the bottom to HA-rich at the top. HA powder (average particle size = 80 μm, Pentax) and Ti powder (average particle size = 68 ± 15 μm, 99.9%, Rare Metallic Co., Ltd., Japan) were used as raw materials. Commercial Ti plates (0.8 mm thick, ASTMB348-GR2) were polished with #400 SiC abrasive paper, washed ultrasonically in acetone and ethyl alcohol, and then dried in air before spraying. The average thickness and surface roughness ($R_a$) of the obtained HA/Ti composite coatings were measured by profilometer (SV-600, Mitsutoyo, Japan) and confocal scanning laser microscope (OLS3000, Olympus). The coatings' bond strength was measured by an autograph-testing machine (AG-500A, Shimadzu, Japan). For this measurement, iron rods 8 mm in diameter were bonded to both the coated and uncoated sides of each sample with epoxy glue (SW 2214, 3 M). A tensile stress was applied to the coating layer at a crosshead speed of 0.5 mm/min. Ti coatings without HA powder were also prepared using various compositions of plasma gas to study reactions between the plasma gas and the Ti powder. The obtained HA/Ti composite and Ti coatings were evaluated by X-ray diffraction (XRD) (MPX,[3] MAC Science, Japan). The coated samples were sectioned with a diamond cut-off wheel, mounted in resin, polished with 1/4 μm diamond paste as a final polishing step, and then chemically etched by 3% HF solution. The sample cross-sections thus prepared were observed by scanning electron microscope (SEM) (S3000N, Hitachi).

Table 1
Experimental conditions

| | |
|---|---|
| Plasma power (kW) | 10–27 |
| Plasma frequency (MHz) | 4 |
| Plasma gas | Argon + 1–6% oxygen or argon + 1–6% nitrogen |
| Flow rate of plasma gas (L/min) | 50 |
| Pressure (Pa) | $6.7 \times 10^4$ |
| Feed rate of HA powder (g/min) | 0–0.1 |
| Feed rate of Ti powder (g/min) | 0.15–0 |
| Carrier gas | Argon |
| Flow rate of carrier gas (L/min) | 5 |
| Spray distance (cm) | 28–35 |

## 3. Results

Fig. 1 shows the bond strength of the HA/Ti composite coatings. When sprayed using Ar–$N_2$ plasma, the bond strength values for the HA/Ti composite coatings were 40 MPa or more. The bond strength showed a tendency to increase with the RF input power. The average bond strength for the HA/Ti composite coatings sprayed with Ar–$N_2$ was 65.5 MPa. However, the HA/Ti composite coatings prepared with Ar–$O_2$ plasma had significantly lower bond strength (under 30 MPa), regardless of the fact that the other processing parameters, such as RF input, substrate temperature and working distance, were almost the same.

Fig. 2 shows a typical SEM image and EDX mappings of a cross-section of our HA/Ti composite coating. The SEM image shows that the HA and Ti grains in the composite coating adhered together well. Small pores and crevices were also observed in the coating layer. Such textures were similarly observed in all our HA/Ti composite coatings regardless of the plasma gas composition during rf-TPS.

Fig. 3 shows typical SEM images obtained of chemically etched cross-sections of the Ti-rich bottom layer in HA/Ti composite coatings prepared with Ar–$O_2$ or Ar–$N_2$ plasma (Fig. 3a and b, respectively). The characteristic lamellar

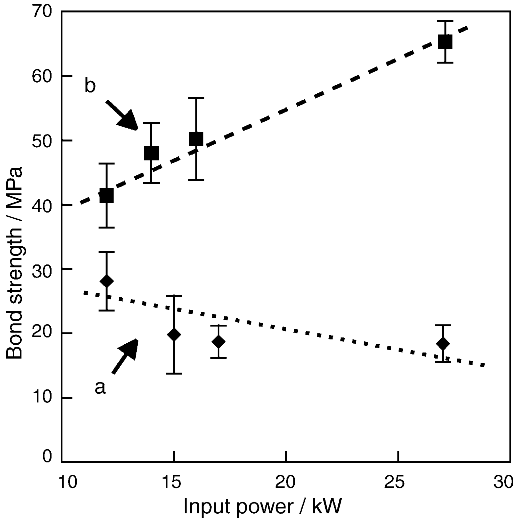

Fig. 1. Bond strength of HA/Ti composite coatings prepared with Ar–$O_2$ plasma (a) or Ar–$N_2$ plasma (b) plotted against input power.

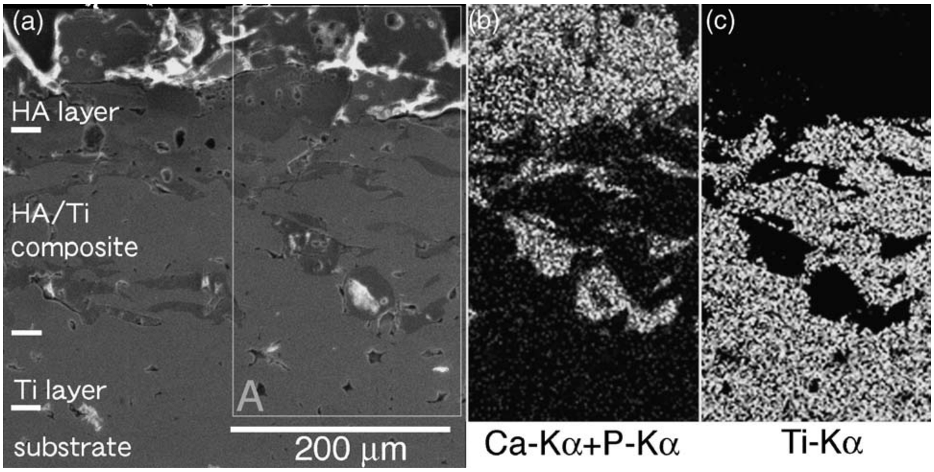

Fig. 2. SEM image (a) and EDX mappings (b and c) of a cross-section of a HA/Ti composite coating prepared with Ar–$N_2$ plasma.

structure of TPS deposits was observed in all the chemically etched cross-sections regardless of the plasma gas composition. However, the structure at the interfaces between the Ti splats differed significantly with the plasma gas composition. When the coatings were sprayed with Ar–$O_2$ plasma, crevice-like structures were observed along the interfaces between the Ti splats (Fig. 3a). Such microstructures were not observed in the cross-sections before chemical etching. An acicular texture can also be observed in magnified SEM images of the chemically etched cross-section of a coating prepared with Ar–$N_2$ plasma (Fig. 3c and d).

Fig. 4 shows XRD patterns of HA/Ti composites (HA = 27 mass%) prepared with Ar–$N_2$ or Ar–$O_2$ plasma. Minute XRD peaks corresponding to tetracalcium phosphate ($Ca_4P_2O_9$, TTCP), tricalcium phosphate ($Ca_3[PO]_4$, TCP) and calcium oxide (CaO) were apparent in all the HA/Ti composites. In addition, a minute XRD peak ascribable to titanium dioxide was observed in the HA/Ti composite prepared with Ar–$O_2$ (Fig. 4a), while peaks ascribable to titanium nitride were seen in the composite prepared with Ar–$N_2$ plasma (Fig. 4b). The formation of these nitride and oxide phases was observed more clearly on Ti coatings prepared without HA powder. The XRD patterns of plasma-sprayed Ti coatings without HA powder, seen in Fig. 5, indicate that $TiO_2$ (rutile phase) was formed on the Ti deposits sprayed with Ar–$O_2$ plasma (Fig. 5a). On the other hand, as shown in

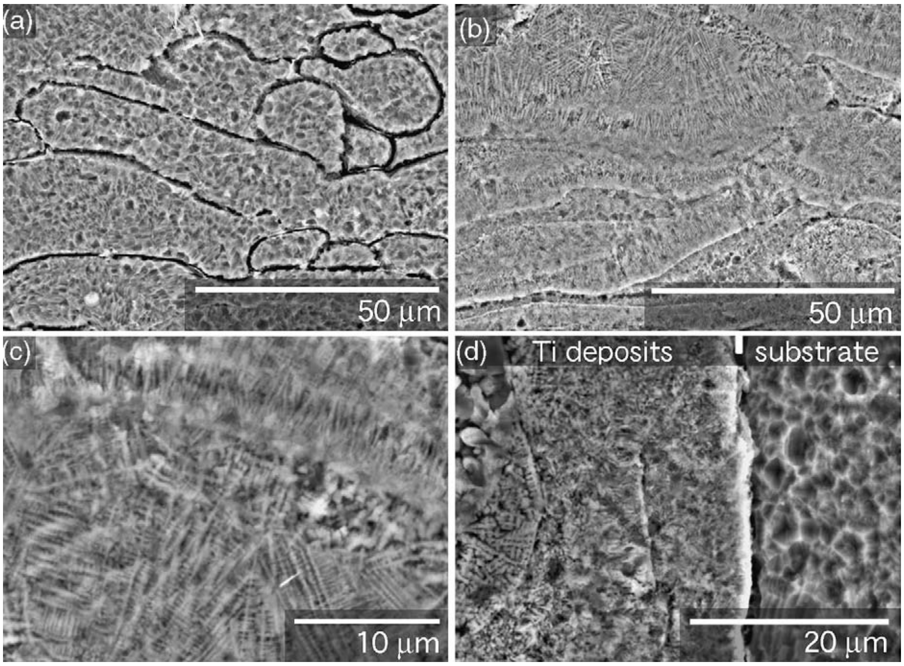

Fig. 3. SEM images of chemically etched cross sections of the Ti-rich bottom layer in HA/Ti composite coatings prepared with Ar–$O_2$ (a) or Ar–$N_2$ (b) plasma. Magnified SEM images of the chemically etched cross section of the Ti-rich layer in a HA/Ti composite coating prepared with Ar–$N_2$ plasma (c and d).

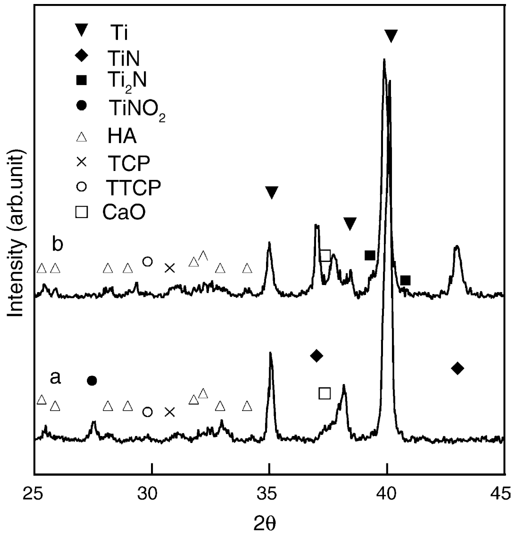

Fig. 4. XRD patterns of HA/Ti composite layers (HA = 27 mass%) plasma-sprayed using Ar–$O_2$ plasma (a) or Ar–$N_2$ plasma (b).

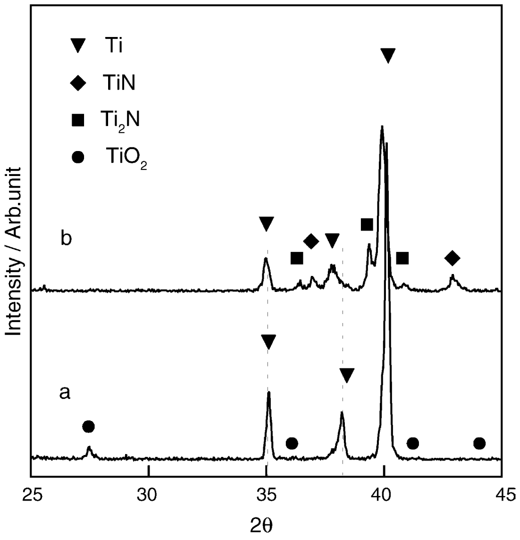

Fig. 5. XRD patterns of Ti coatings (without HA) plasma-sprayed with Ar–$O_2$ plasma (a) or Ar–$N_2$ plasma (b).

Fig. 5b, minute X-ray peaks ascribable to TiN or $Ti_2N$ were observed when the coating was sprayed with Ar–$N_2$ plasma. Peak shifts of the titanium (1 0 0), (0 0 2) and (1 0 1) planes were also observed in Fig. 5a.

## 4. Discussion

Considering the low mechanical strength of HA compared with Ti, the mechanical strength of the Ti networks in a HA/Ti composite may significantly affect the bond strength of the composite coating. As confirmed by SEM observation, HA/Ti composite coatings prepared by Ar–$O_2$ and Ar–$N_2$ plasma differed in their microstructure—particularly at the interfaces between Ti splats.

As seen in Fig. 3c and d, the Ti/Ti interfaces in coatings prepared with Ar–$N_2$ were compacted. On the contrary, crevice-like structures were observed at the interfaces between Ti splats prepared with Ar–$O_2$ plasma (Fig. 3a). As confirmed by XRD measurements (Figs. 4 and 5), $TiO_2$ formed on the Ti deposits prepared with Ar–$O_2$ plasma. Therefore, the crevice-like structures observed in the HA/Ti composite coatings prepared with Ar–$O_2$ plasma probably formed by dissolution of the thin $TiO_2$ layer in the corresponding regions during chemical etching.

As seen in Fig. 3c and d, an acicular texture was observed in the Ti splats prepared with Ar–$N_2$ plasma. Analogous structures have been reported with the plasma nitriding of titanium surfaces using a dc arc plasma jet to create a titanium nitride layer.[12,13] According to these reports, such acicular textures were observed in nitrogen diffusion regions. Our XRD patterns of Ti deposits prepared with Ar–$N_2$ plasma indicate that titanium nitride phases formed on the Ti deposits (Fig. 4b). In addition, X-ray peaks ascribable to titanium (1 0 0), (0 0 2) and (1 0 1) planes shifted to lower angles. This implies an increase in the average lattice parameter of α-titanium in the Ti deposits sprayed with Ar–$N_2$ plasma, suggesting that titanium–nitrogen solid solution formed in the deposited Ti splats. In such solid solution, dissolved nitrogen exists at interstitial positions in the α-titanium lattice and causes deformations in the α-titanium cells.[14] Thus, the acicular texture observed on the Ti splats sprayed with Ar–$N_2$ plasma probably corresponds to the formation of titanium–nitrogen solid solution. In the present study, such acicular textures did not appear in the Ti substrate near the coating/substrate interface—not even after pre-heating the substrate with the plasma jet for 2 min before spraying (Fig. 3d). Therefore, this suggests that the titanium nitrides on the Ti particles were mainly formed in the plasma jet while in-flight.

In general, the nitriding of a metal surface improves its mechanical properties. For instance, the hardness of titanium nitrides and titanium–nitrogen solid solution is higher than that of pure titanium.[15,16] Moreover, titanium nitrides coated by reactive plasma spraying exhibit high resistance to wear.[17,18] This suggests that the partial nitriding of the Ti splats in HA/Ti composite coatings improves the mechanical properties of the Ti networks in the HA/Ti composite and increases the bond strength of such coatings.

In our XRD measurements, no evidence of the formation of oxygen–titanium solid-solution appeared. Moreover, no microstructures indicating the formation of diffusion layers were observed on the Ti splats (Fig. 3a). Our SEM images imply that the excited species in the Ar–$O_2$ plasma reacted only at the surface of the Ti particles, and formed a thin $TiO_2$ layer on this surface in the plasma. Subsequently, such Ti particles deposited on the Ti splats on the substrate and formed a thin $TiO_2$ layer at the interfaces between the splats. The formation of such a thin $TiO_2$ layer between the Ti splats probably reduces the mechanical strength of the Ti network in the HA/Ti composite coatings. These SEM observations suggest that the significant difference in the bond strength between the coatings prepared with $Ar–N_2$ and $Ar–O_2$ plasmas (Fig. 1) arose from the difference in the microstructure at the Ti/Ti interfaces.

It appears that the by-products seen in the XRD patterns of the HA/Ti composite layers (i.e., TTCP, TCP and CaO; Fig. 4) were formed by thermal decomposition of the HA powder in the plasma, as reported in previous studies.[1–4,7,9,19] Reactions between HA and Ti particles contacting each other in the plasma flame might form some titanium–calcium compounds. However, no clear peaks corresponding to such titanium–calcium compounds were observed in the XRD patterns of our HA/Ti composite coatings. This implies that the amount of by-products due to side reactions occurring between the HA and Ti powders was undetectable and therefore such side reactions may be ignored.

## 5. Conclusions

Our results clearly revealed that the composition of the plasma gas during rf-RPS plays a crucial role in improving the adhesiveness of HA/Ti composite coatings. We investigated in situ reactions of Ti particles by making use of titanium's high reactivity in the plasma flame. rf-RPS with $Ar–N_2$ plasma allowed the formation of HA/Ti composite coatings with excellent adhesion to the titanium substrate. Indeed, ca. 150 μm thick HA/Ti composite coatings sprayed at 27 kW using $Ar–N_2$ plasma had a bond strength of 65.3 MPa, whereas that of 150 μm thick coatings sprayed with $Ar–O_2$ plasma at similar input power was only about 20 MPa. As confirmed by XRD, rf-RPS with $Ar–N_2$ and $Ar–O_2$ plasma produced titanium nitride and titanium dioxide, respectively, in titanium deposits. SEM observations showed that the microstructures at the interfaces between the Ti splats differed drastically according to the type of plasma gas used during rf-RPS. The influence of the plasma gas composition on the microstructure of the Ti deposits in HA/Ti composites is likely to directly affect the bond strength of HA/Ti composite coatings.

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